

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08J 9/12, 9/18	A1	(11) International Publication Number: WO 95/23181 (43) International Publication Date: 31 August 1995 (31.08.95)
(21) International Application Number: PCT/FI95/00090 (22) International Filing Date: 22 February 1995 (22.02.95) (30) Priority Data: 940876 25 February 1994 (25.02.94) FI (71) Applicant (for all designated States except US): VALTION TEKNILLINEN TUTKIMUSKESKUS (FI/FI); c/o Otatech Ltd., P.O. Box 402, FIN-02151 Espoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): AALTONEN, Olli (FI/FI); Eino- Leinon Katu 10 A 10, FIN-00250 Helsinki (FI). QVINTUS-LEINO, Pia (FI/FI); Päivänkajontie 8 K, FIN- 02210 Espoo (FI). (74) Agent: HARTIKAINEN, Liisa; Otatech Ltd., P.O. Box 402, FIN-02151 Espoo (FI).	(81) Designated States: CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>	
(54) Title: MICROPOROUS CELLULOSE DERIVATIVES AND A METHOD FOR PRODUCING THE SAME (57) Abstract A cellulose derivative, for example in the form of film, fibers or particles, is brought to contact with carbon dioxide, preferably at 100 to 400 bar pressure and 50 to 100 °C temperature. Carbon dioxide can contain a small amount of additives, such as alcohols. Cellulose derivative swells by the effect of pressurized carbon dioxide. After a certain swelling period the pressure of carbon dioxide is very rapidly reduced causing the cellulose derivative to foam. Depending on the chosen conditions one obtains microporous cellulose derivative material with an average pore size from 0.5 to 50 micrometers. The micropores can be open or closed and their distribution in the foamed material can be adjusted as preferred by changing treatment conditions. Microporous cellulose derivatives can be used for example as support materials for catalysts, enzymes or selective antibodies in immunochromatography. Other applications include ultra light structure materials and microfilters.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

MICROPOROUS CELLULOSE DERIVATIVES AND A METHOD FOR PRODUCING THE SAME.

5 The invention relates to new microporous materials, which are made of cellulose derivatives. The cellulose derivatives related to the invention have such molecular weight, substituents and degree of substitution that they are essentially insoluble in water. The materials related to the invention are also characterized by having a pore size from 0.5 to 10 50 micrometers.

10 The invention also relates to a new method for making microporous cellulose derivative materials. It is characteristic to the new method that cellulose derivative is swelled by bringing it in contact with a high pressure carbon dioxide, preferentially at supercritical state. After the swelling at elevated pressure the pressure of the carbon dioxide which is in 15 contact with the cellulose derivative is quickly reduced so that a microporous material is formed.

20 Porous materials made of cellulose derivatives are used, for example, as ion exchange resins and filters for tobacco smoke. The previously known porous cellulose derivatives are characterized by a large, over 100 micrometer, average pore size and a very uneven pore size distribution. According to previously known methods, the foaming of cellulose derivatives is made by using foaming agents which are mixed with the cellulose derivative melt or solution. Such foaming agents can be inorganic, gas-forming salts or inert, bubble 25 forming gases which are blown to the melt or solution. It is often necessary to use softeners for cellulose derivatives and a high foaming temperature.

30 It is known from patent publication BE 874772, for example, to make cellulose acetate foam by melting cellulose acetate with a softener, crystallization centers and a foaming agent and to extrude the melt to obtain formed articles. The patent publication describes cigarette filters as an application for the obtained product.

35 Microporous cellulose derivatives have a much wider application area than the known porous materials which are made from cellulose derivatives. By microporous materials we here mean materials which have an average pore size smaller than approximately 100 micrometers. Moreover, in many applications it is important that the pore- or particle size distribution is very sharp. Application areas for microporous, open-pore cellulosic derivatives are, for example, biologically degradable microfilters for separating pathogens and other micro-organisms from air or water, porous supports for immobilized enzymes, 40 support materials for catalysts, adsorbents for immobilizing cells in many medicinal applications and porous materials coated with selective antibodies for quick diagnostics, such as immunochromatography. Closed pore structured, microporous cellulose derivatives again can function e.g. as ultralight building materials or as support matrices for slow-acting pharmaceuticals or agrochemicals.

45 From patent publication US 5 158 986 it is known to make closed-pore, microporous material from thermoplastic, synthetic polymers by treating them with pressurized, supercritical carbon dioxide and by then letting the carbon dioxide pressure decrease rapidly. In the described method the foamed material can be PVC, polyetheneterphthalate 50

or polyethene. The foaming time in the described method changes from 20 seconds to 2 minutes and the average pore sizes are in the area from 0.1 to 2.0 micrometers.

5 From patent publication PCT/EP90/01895 it is known to make porous materials from synthetic, biodegradable polymers by treating them also with supercritical carbon dioxide and by letting the carbon dioxide pressure then to decrease rapidly. By using the described method one can produce foamed materials from polylactides, polyglycolides and their
10 co-polymers. The pressure reduction time described in the patent publication is 10 seconds.

We have now discovered that, deviating from the previously known methods, by selecting the treating conditions exactly right, one can produce microporous materials from cellulose derivatives by pressurizing cellulose derivatives in supercritical carbon dioxide and
15 subsequently reducing the pressure rapidly.

In accordance with the present invention a derivative, such as an ester or an ether, made from a natural polymer, such as cellulose, for example in the form of film, fibers or particles is brought to contact with high pressure carbon dioxide. Carbon dioxide pressure,
20 temperature and the pressurization time of the cellulose derivative in carbon dioxide are chosen according to the composition, dimensions of the cellulose derivative and the preferred result so that high pressure carbon dioxide penetrates in the solid cellulose derivative which then swells. Additives, such as small molecular weight alcohols, organic acids or esters can be added to carbon dioxide, when needed. In accordance with the
25 invention the pressure of the cellulose derivative, which has been swollen in high pressure carbon dioxide, is rapidly reduced, so that porous material is obtained after the pressure reduction. The pressure reduction can be accomplished for example by letting the carbon dioxide, which is in contact with the cellulose derivative, to expand into lower pressure. The pressure reduction rate and the final pressure of carbon dioxide are chosen so that
30 desired microporous cellulose derivative material is obtained.

The invention makes possible new materials, made of cellulose derivatives, which, apart from previously known materials, have smaller average pore size and narrower pore size distribution. The invention also makes it possible to produce either closed- or open-cell
35 cellulose derivative materials. Furthermore the invention makes it possible to produce porous cellulose derivative materials which are either uniformly porous or alternatively materials which have, for example, a denser skin and a more porous core. Thus the invention provides, for example, hollow fibers or fibers with a very porous core.

40 An advantage provided by the microporous cellulose derivatives in accordance with the invention, is improved product quality, especially improved capacity and selectivity in applications where porous cellulose derivatives are used, for example, as carriers for catalysts, enzymes or proteins or as adsorption materials.

45 An advantage provided by the production method of microporous cellulose derivatives in accordance with the invention, is the reduction or elimination of the use of flammable or toxic organic solvents. The production method in accordance with the invention also provides increased rate of manufacturing process as an advantage.

50

The following examples describe the materials and method for producing them in accordance with the invention. However, the scope of the invention is not restricted to the materials and methods for producing them which are described in the following examples.

Example 1.

- 10 A piece of colourless, transparent film made of cellulose acetate (acetyl substitution 2.45 mol/mol, molecular weight ca. 61 000) was placed in a 40 ml pressure vessel. The initial thickness of the film was 0.13 mm. The film was placed inside a pressure vessel, in a basket made of metal net so, that it does not touch the wall or bottom of the vessel. The pressure vessel was closed and heated with an external electric heater to 50 C. Carbon dioxide was brought to the vessel from a reservoir bottle so, that the pressure inside the vessel increased to ca. 70 bar. The pressure vessel was heated and carbon dioxide was pumped to the vessel with a compressor so, that the final pressure became 208 bar and temperature 80 C. Cellulose acetate film was kept in the pressurized vessel for 90 minutes after which a ball valve at the bottom of the vessel was quickly opened. The carbon dioxide in the vessel was discharged to atmospheric pressure so, that the cellulose acetate film remained inside the vessel.

After pressure reduction, the cellulose acetate film was opaque and white. Its thickness had increased to 0.17 mm, 31 %, in the treatment. Electronic microscopic inspection revealed that the cross section of the cellulose acetate film was porous. The pores were almost round, closed and their average diameter was 9 micrometers.

Example 2.

- 30 In the experimental set up described in example 1, the pressure of carbon dioxide was changed between 100 - 308 bar and temperature between 50 - 92 C. The treatment conditions and results are compiled in the next table.

Exp No.	Pressure bar	Tempera- ture C	Ethanol- concentra- tion weight-%	Butyl acetate concentra- tion weight-%	Pressure reduction time seconds	Film thick- ness µm	Film structure	Average pore size µm
0						133	solid	0
1	185	72	0	0	0.2	105	solid	0.1
2	209	87	1	0.5	0.2	152	solid	0.3
3	280	81	1	0	0.1	132	solid	0
4	217	79	0	6	0.1	102	solid	30
5	205	85	2	0	0.2	145	closed pores	1
6	288	71	6	0.5	0.2	117	closed pores	8
7	259	81	6	1	0.3	152	closed pores	5

4

	8	193	90	6	6	0.1	245	open pores	6
5	9	100	50	12	1	0.1	140	closed pores	0.5
	10	308	92	15	0	0.1		closed pores	31
	11	212	70	6	0	0.1	276	closed pores	14
10	12	215	80	15	0	0.08	169	partly open pores	13
	13	167	70	15	0	0.09	136	closed pores	9
	14	248	80	4	0	0.1	335	closed pores	18
	15	221	71	6	0	0.1	470	closed pores	15
15	16	240	70	8	0	0.1	511	closed pores	24
	17	212	90	6	0	0.08	500	open pores	50

20 In some of the pressurization-pressure reduction experiments ethyl alcohol and butyl acetate were added to carbon dioxide. The concentrations of the additives were varied. Moreover, the pressure reduction rate of carbon dioxide was varied by partly closing the tube, which leads out from the pressure vessel, with a valve. The pressure reduction time in the table is the time during which the carbon dioxide pressure has been reduced from the

25 initial pressure to approximately 40 bars. From there on the pressure reduction rate slows down because of carbon dioxide liquefaction. The experiments, which are described in the example, show that microporous cellulose acetate film is obtained only at certain treatment conditions. Moreover, the porosity of the cellulose acetate film, the open- or closed pore structure and the pore size depend strongly on treatment conditions.

30

Example 3.

In the experimental set-up described in example 1, n-propylalcohol was used as an additive in carbon dioxide. 5 weigh-% propanol was added to carbon dioxide. 133 micrometer thick

35 cellulose acetate film was pressurized in carbon dioxide at 220 bars and 80 C. After rapid pressure reduction foamed cellulose-acetate film was obtained. The thickness of the obtained film was 230 micrometers. The surface of the microporous film was solid and the core of the film was thoroughly foamed. The average diameter of the pores was 16 micrometers.

40

Example 4.

In the experimental set-up described in example 1, a piece of clear cellulose triacetate film was placed in the pressure vessel. The film was prepared by dissolving cellulose triacetate

45 (acetyl substitution ca. 3 mol/mol and molecular weight ca. 73 000) in methylene chloride solution and by letting the solvent evaporate slowly. The triacetate film was pressurized in carbon dioxide at 400 bars and at 80 C. 5 weight-% ethanol was added to carbon dioxide. After rapid pressure reduction a white, opaque cellulose triacetate film was obtained.

50

Example 5.

- 5 In the experimental set-up described in example 1, a piece of cellulose acetate fabric was placed in the pressure vessel. The diameter of a single filament in the fabric was ca. 18 micrometers. The acetate fabric was pressurized in carbon dioxide at 208 bars and at 75 C. 5 weight-% butyl alcohol was added to carbon dioxide. After rapid pressure reduction a fabric was obtained where the filaments had a solid skin but porous core. The average pore size was ca. 3 micrometers. Filament diameters remained essentially unaltered during carbon dioxide treatment.

Example 6.

- 15 In the experimental set-up described in example 1, ethyl cellulose powder was placed in the pressure vessel. The ethyl substitution degree in the material was ca. 2.5 mol/mol. Ethyl cellulose powder was pressurized with carbon dioxide at 290 bars and 70 C. After rapid pressure reduction ethyl cellulose powder was obtained where particle diameter had increased approximately 30 %. Electron microscopic study revealed that carbon dioxide treatment had made the particles porous.

Example 7.

- 25 A piece of 130 micrometer thick, clear, colourless, cellulose acetate film was placed in a pressure vessel which had a volume of 200 ml. The film was placed in a rack so that it did not touch either the walls or bottom of the pressure vessel. Liquid methanol was measured at the bottom of the pressure vessel. It was heated and carbon dioxide was led into the vessel so, that the final pressure became 220 bars and the final temperature 81 C. The concentration of methanol in carbon dioxide became 5 weight-% under these conditions.
- 30 After 45 minutes a needle valve at the cover of the pressure vessel was opened quickly. Carbon dioxide discharged from the vessel to atmospheric pressure. Pressure reduction inside the vessel occurred during ca. 7 seconds. A white, opaque, porous cellulose acetate film was obtained. The thickness of the film had increased to approximately 180 micrometers. The cross-section of the film was porous in a way that the pores at the film surface were very small and their diameter increased towards the core. The diameter of
- 35 largest pores was ca. 50 micrometers.

40

45

50

Claims:

- 5
1. Microporous, water insoluble cellulose derivative materials characterized in that cellulose derivative is brought to contact with a substance which mainly consists of carbon dioxide, at elevated temperature and pressure, after which the pressure of the substance
- 10 derivative, is quickly reduced, preferably over a period of less than ten seconds so that such microporous cellulose derivative material is obtained where the average pore diameter is from 0.5 to 50 micrometers.
- 15 2. Materials according to claim 1 wherein the cellulose derivative is a cellulose ester or a cellulose ether with a degree of substitution from 2.4 to 3.0.
3. A method according to claim 1 wherein the pores of the microporous cellulose derivative material are open.
- 20 4. A method according to claim 1 wherein the pores of the microporous cellulose derivative material are closed.
5. A method for producing microporous materials from cellulose derivatives comprising the steps of bringing the cellulose derivative in contact with a substance, which mainly
- 25 consists of carbon dioxide, at elevated pressure and temperature, after which the pressure of the substance which mainly consists of carbon dioxide and which is in contact with the cellulose derivative, is quickly reduced, preferably over a period of less than ten seconds so that microporous cellulose derivative material is obtained.
- 30 6. A method according to claim 5 wherein the cellulose derivative is brought to contact with a substance which mainly consists of carbon dioxide at 100 to 400 bar pressure and at 50 to 100 C temperature.
- 35 7. A method according to claim 5 wherein a small molecular alcohol or an ester is added to the carbon dioxide which is in contact with the cellulose derivative material.
8. A method according to claims 5 and 7 wherein the amount of small molecular alcohol or ester in the carbon dioxide which is in contact with the cellulose derivative, is from 1 to
- 40 15 weight-%.
9. A method according to claim 5 wherein the pressure of the compound which mainly consists of carbon dioxide and which is in contact with the cellulose derivative, is reduced to essentially lower pressure within a period of 0.08 to 7 seconds.
- 45 10. A method according to claim 5 wherein the cellulose derivative is either cellulose ester or cellulose ether where the degree of substitution is from 2.4 to 3.0.
- 50

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 95/00090

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08J 9/12, C08J 9/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA, WPI, IFIPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A2, 0376064 (TOYO ENGINEERING CORPORATION), 4 July 1990 (04.07.90)	1,5-7
A	--	2-4,8-10
X	WO, A1, 9109079 (FARMITALIA CARLO ERBA S.R.L.), 27 June 1991 (27.06.91)	1,5,6
A	--	2-4,7-10
X	US, A, 5158986 (SUNG W. CHA ET AL), 27 October 1992 (27.10.92)	1,5,6
A	--	2-4,7-10

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *B* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z document member of the same patent family

Date of the actual completion of the international search

19 May 1995

Date of mailing of the international search report

14 -06- 1995

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Eva Johansson
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 95/00090

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0610953 (MINNESOTA MINING AND MANUFACTURING COMPANY), 17 August 1994 (17.08.94) --	1-10
A	STN International, File CA, Chemical Abstracts, volume 96, no. 18, 3 May 1982, (Columbus Ohio, US), Grebennikov, S.F. et al: "Pore structure and adsorption properties of activated carbon fibers", abstract no. 144356 & Khim. Volokna (1982), (1), 38-9 --	1-10
A	STN International, File CA, Chemical Abstracts, volume 85, no. 8, 23 August 1976, (Columbus, Ohio, US), McEnaney, Brian et al: "The development of porosity in heat-treated polymer carbons upon activation by ***carbon*** ***dioxide***", abstract no. 52084, & Carbon (1975), 13(6), 515-19 -- -----	1-10

INTERNATIONAL SEARCH REPORT
Information on patent family members

01/04/95

International application No.
PCT/FI 95/00090

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0376064	04/07/90	JP-A- 2160842 US-A- 5133913	20/06/90 28/07/92
WO-A1- 9109079	27/06/91	EP-A,B- 0464163 JP-T- 4505775	08/01/92 08/10/92
US-A- 5158986	27/10/92	CA-A- 2107355 EP-A,A- 0580777 JP-T- 6506724 US-A- 5334356 WO-A- 9217533	06/10/92 02/02/94 28/07/94 02/08/94 15/10/92
EP-A1- 0610953	17/08/94	NONE	